

ATTENT COOPERATION TRAD. & TTY

PCT

NOTIFICATION OF ELECTION  
(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C.20231  
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

|   |   |
|---|---|
| Date of mailing:<br><b>28 September 2000 (28.09.00)</b>       |   |
| International application No.:<br><b>PCT/AU00/00224</b>       | Applicant's or agent's file reference:<br><b>00638WO/AM</b> |
| International filing date:<br><b>22 March 2000 (22.03.00)</b> | Priority date:<br><b>22 March 1999 (22.03.99)</b>           |
| Applicant:<br><b>SULLIVAN, Leigh, Albert et al</b>            |   |

1. The designated Office is hereby notified of its election made:

in the demand filed with the International preliminary Examining Authority on:

**13 June 2000 (13.06.00)**

in a notice effecting later election filed with the International Bureau on:

**\_\_\_\_\_**

2. The election  was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

|   |  |
|---|--|
| The International Bureau of WIPO<br>34, chemin des Colombettes<br>1211 Geneva 20, Switzerland<br>Facsimile No.: (41-22) 740.14.35 | Authorized officer:<br><b>J. Zahra</b><br>Telephone No.: (41-22) 338.83.38 |
|---|--|

## PATENT COOPERATION TREATY

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

|  |   |   |
|--|---|---|
| Applicant's or agent's file reference<br>00638WO/AM    | <b>FOR FURTHER ACTION</b>   | see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below. |
| International application No.<br><b>PCT/AU00/00224</b> | International filing date ( <i>day/month/year</i> )<br><b>22 March 2000</b> | (Earliest) Priority Date ( <i>day/month/year</i> )<br><b>22 March 1999</b>  |
| Applicant<br><b>RISATEC PTY LIMITED et al</b>          |   |   |

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

It is also accompanied by a copy of each prior art document cited in this report.

**Basis of the report**

- a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing:

contained in the international application in written form.

filed together with the international application in computer readable form.

furnished subsequently to this Authority in written form.

furnished subsequently to this Authority in computer readable form.

the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

Certain claims were found unsearchable (See Box I).

3.  Unity of invention is lacking (See Box II).

4. With regard to the title,  the text is approved as submitted by the applicant.

the text has been established by this Authority to read as follows:

5. With regard to the abstract,  the text is approved as submitted by the applicant

the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No. 2

as suggested by the applicant.

None of the figures

because the applicant failed to suggest a figure

because this figure better characterises the invention

**Box III TEXT OF THE ABSTRACT (Continuation of item 5 of the first sheet)**

An apparatus for measuring the reduced inorganic sulfur content of a sample. The apparatus has a reaction chamber (12) and means (14) for introducing a reducing agent that can selectively convert the reduced inorganic sulfur of a sample in the reaction chamber (12) to hydrogen sulfide. The reducing agent can be chromous chloride. The apparatus also includes means for measuring the amount of hydrogen sulfide evolved by reaction of the reducing agent with the sample and a detector for detecting when evolution of the hydrogen sulfide has reduced or ceased.

The term 'reduced inorganic sulfur' refers to sulfur in a form that can undergo oxidation and includes mineral sulphides and elemental sulfur.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU00/00224

**A. CLASSIFICATION OF SUBJECT MATTER**

Int. Cl. ? G01N 31/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**Minimum documentation searched (classification system followed by classification symbols)  
G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
DWPI and JAPIO with keywords: sulf(ph)ur, 'hydrogen sulf(ph)ide', H2S, mineral, meas+, assay, analy+**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                 | Relevant to claim No. |
|-----------|--|-----------------------|
| A         | Derwent Abstracts Accession No. 91-162504/22, Class S03,<br>SU 1578-672 A (GEOCHEM MIN) 15 July 1990               |                       |
| A         | Derwent Abstracts Accession No. 97-090521/09, Class J04 M24,<br>JP 08327625 A (NIPPON STEEL CORP) 13 December 1996 |                       |

Further documents are listed in the continuation of Box C     See patent family annex

## \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search  
**17 May 2000**Date of mailing of the international search report  
**29 MAY 2000**

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE  
PO BOX 200, WODEN ACT 2606, AUSTRALIA  
E-mail address: pct@ipaaustralia.gov.au  
Facsimile No. (02) 6285 3929

Authorised officer

**ROSS BURDON**  
Telephone No : (02) 6283 2605

Tue May 16 16:26:57, VIEWED UNLINKED

AUGE = \* S03

91-162504/22 \* SU 1578-672-A

Sulphur deposits prospecting - by extracting hydrogen sulphide from samples of gypsum and anhydrite by heating up to bitumen destruction temp.

AS UKR GEOCHEM MIN 26.06.87-SU-269305

J04 (15.07.90) G01v-09

26.06.87 as 269305 (967AS)

The method involves taking samples, extrn. of gypsum and anhydrite and their subsequent analysis. For efficiency, the process includes extracting hydrogen sulphide from the gypsum and anhydrite by heating to temp. of destruction of bitumens. The presence of the sulphur deposits is indicated when the conc. of hydrogen sulphide exceeds 0.025 molar proportion.

USE/ADVANTAGE - In prospecting mineralogy in geological-mineralogical work for searching and prospecting minerals deposits. Improved efficiency is obtd. Bul.26/15.7.90 (2pp Dwg.No.0/0)

N91-124411

83-C4

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US Office: Derwent Inc., 1313 Dolley Madison Boulevard,  
Suite 303, McLean, VA22101, USA  
Unauthorised copying of this abstract not permitted.

**97-090521/09**      J04 M24  
NIPPON STEEL CORP  
95.06.05 95JP-138293 (96.12.13) G01N 33/20, 25/02, 31/00  
Carbon, sulphur and phosphorus analysis for high efficiency and  
speed - by measuring carbon content by temp fused sample metal  
change, and supplying reducing acid and generating hydrogen  
sulphide and phosphine gas  
**C97-029436**

YAWA 95.06.05  
\*JP 08327625-A

J(4-C3) M(24-A6)

Content of C is measured by the temp change of fused sample metal,  
and contents of S and P are measured by supplying reducing acid to  
the fused metal sample, and generated H<sub>2</sub>S and PH<sub>3</sub> gases are  
determined by each test paper.

USE      Analysis of C, S and P.

ADVANTAGE  
C, S and P are analysed efficiently and in a short time.  
(6pp082DwgNo.0/2)

JP 08327625-A

**PATENT COOPERATION TREATY**  
**PCT**  
**INTERNATIONAL PRELIMINARY EXAMINATION REPORT**

REC'D 30 JUN 2000

WIPO

PCT

(PCT Article 36 and Rule 70)

|   |  |  |
|---|--|--|
| Applicant's or agent's file reference<br>00638WO/AM   | <b>FOR FURTHER ACTION</b>  | See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416). |
| International application No.<br>PCT/AU00/00224   | International filing date ( <i>day/month/year</i> )<br>22 March 2000 | Priority Date ( <i>day/month/year</i> )<br>22 March 1999   |
| International Patent Classification (IPC) or national classification and IPC<br><b>Int. Cl.</b> <sup>7</sup> G01N 33/24 31/00 |  |  |
| Applicant<br>RISATEC PTY LIMITED et al  |  |  |

|  |   |   |    |                                   |     |   |    |   |   |   |    |  |     |   |      |  |
|--|---|---|----|-----------------------------------|-----|---|----|---|---|---|----|--|-----|---|------|--|
| 1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.  |   |   |    |                                   |     |   |    |   |   |   |    |  |     |   |      |  |
| 2. This REPORT consists of a total of 3 sheets, including this cover sheet.<br><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).<br>These annexes consist of a total of sheet(s).   |   |   |    |                                   |     |   |    |   |   |   |    |  |     |   |      |  |
| 3. This report contains indications relating to the following items:   |   |   |    |                                   |     |   |    |   |   |   |    |  |     |   |      |  |
| <table> <tr> <td>I</td> <td><input checked="" type="checkbox"/> Basis of the report</td> </tr> <tr> <td>II</td> <td><input type="checkbox"/> Priority</td> </tr> <tr> <td>III</td> <td><input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</td> </tr> <tr> <td>IV</td> <td><input type="checkbox"/> Lack of unity of invention</td> </tr> <tr> <td>V</td> <td><input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</td> </tr> <tr> <td>VI</td> <td><input type="checkbox"/> Certain documents cited</td> </tr> <tr> <td>VII</td> <td><input type="checkbox"/> Certain defects in the international application</td> </tr> <tr> <td>VIII</td> <td><input type="checkbox"/> Certain observations on the international application</td> </tr> </table> | I   | <input checked="" type="checkbox"/> Basis of the report | II | <input type="checkbox"/> Priority | III | <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability | IV | <input type="checkbox"/> Lack of unity of invention | V | <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement | VI | <input type="checkbox"/> Certain documents cited | VII | <input type="checkbox"/> Certain defects in the international application | VIII | <input type="checkbox"/> Certain observations on the international application |
| I  | <input checked="" type="checkbox"/> Basis of the report   |   |    |                                   |     |   |    |   |   |   |    |  |     |   |      |  |
| II   | <input type="checkbox"/> Priority   |   |    |                                   |     |   |    |   |   |   |    |  |     |   |      |  |
| III  | <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability   |   |    |                                   |     |   |    |   |   |   |    |  |     |   |      |  |
| IV   | <input type="checkbox"/> Lack of unity of invention   |   |    |                                   |     |   |    |   |   |   |    |  |     |   |      |  |
| V  | <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement |   |    |                                   |     |   |    |   |   |   |    |  |     |   |      |  |
| VI   | <input type="checkbox"/> Certain documents cited  |   |    |                                   |     |   |    |   |   |   |    |  |     |   |      |  |
| VII  | <input type="checkbox"/> Certain defects in the international application   |   |    |                                   |     |   |    |   |   |   |    |  |     |   |      |  |
| VIII   | <input type="checkbox"/> Certain observations on the international application  |   |    |                                   |     |   |    |   |   |   |    |  |     |   |      |  |

|   |  |
|---|--|
| Date of submission of the demand<br>13 June 2000  | Date of completion of the report<br>23 June 2000                             |
| Name and mailing address of the IPEA/AU<br><br>AUSTRALIAN PATENT OFFICE<br>PO BOX 200, WODEN ACT 2606, AUSTRALIA<br>E-mail address: pct@ipaaustralia.gov.au<br>Facsimile No. (02) 6283 3929 | Authorised Officer<br><br><b>ROSS BURDON</b><br>Telephone No. (02) 6283 2605 |

**L Basis of the report**

1. With regard to the elements of the international application:\*
- the international application as originally filed.
- the description,      pages 1 - 10 as originally filed,  
                              pages filed with the demand,  
                              pages received on with the letter of
- the claims,      pages 11 - 13 as originally filed,  
                              pages as amended (together with any statement) under Article 19,  
                              pages filed with the demand,  
                              pages received on with the letter of
- the drawings,      pages 1/2 - 2/2 as originally filed,  
                              pages filed with the demand,  
                              pages received on with the letter of
- the sequence listing part of the description:  
                              pages as originally filed  
                              pages filed with the demand  
                              pages received on with the letter of
2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.  
These elements were available or furnished to this Authority in the following language which is:
- the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).  
 the language of publication of the international application (under Rule 48.3(b)).  
 the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).
3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, was on the basis of the sequence listing:
- contained in the international application in written form.  
 filed together with the international application in computer readable form.  
 furnished subsequently to this Authority in written form.  
 furnished subsequently to this Authority in computer readable form.  
 The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
 The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished
4.  The amendments have resulted in the cancellation of:  
 the description,      pages  
 the claims,          Nos.  
 the drawings,        sheets/fig.
5.  This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\*

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\* Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. Statement**

|                               |                |     |
|-------------------------------|----------------|-----|
| Novelty (N)                   | Claims 1 - 26  | YES |
|                               | Claims - nil - | NO  |
| Inventive step (IS)           | Claims 1 - 26  | YES |
|                               | Claims - nil - | NO  |
| Industrial applicability (IA) | Claims 1 - 26  | YES |
|                               | Claims - nil - | NO  |

**2. Citations and explanations (Rule 70.7)**

The following documents identified in the International Search Report have been considered for the purposes of this report:

SU 1578-672  
JP 08327625

**Novelty (N) & Inventive Step (IS)**

All the documents cited in the ISR were category A only. Therefore the claimed invention is not disclosed in any of these patent documents and hence all the claims are novel.

The claimed invention is not obvious in the light of any of the cited documents nor disclosed in any obvious combination, nor would the claimed invention be obvious to a person skilled in the art in the light of common general knowledge by itself or in combination with any of these documents.

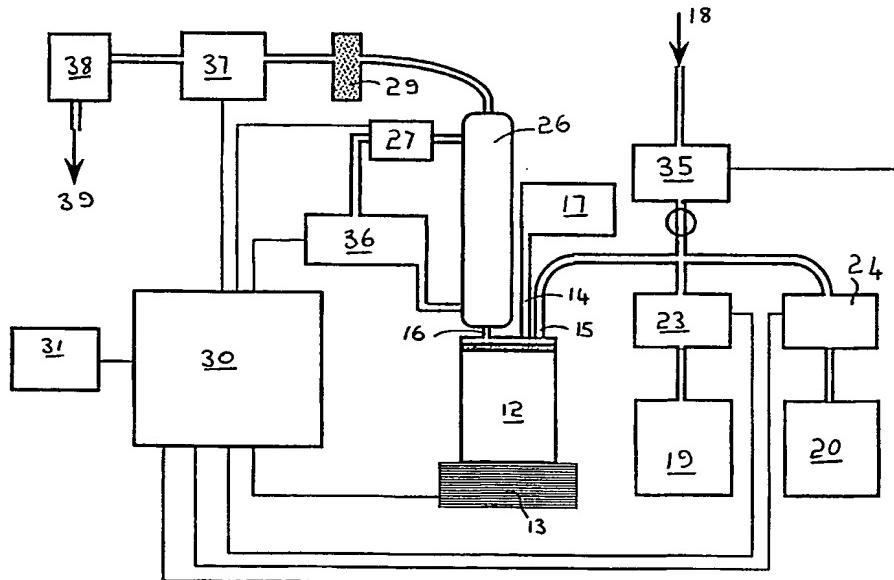


## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

|   |           |   |
|---|-----------|---|
| (51) International Patent Classification 7 :<br><b>G01N 31/00</b> | <b>A1</b> | (11) International Publication Number: <b>WO 00/57174</b>         |
|   |           | (43) International Publication Date: 28 September 2000 (28.09.00) |

|   |  |
|---|--|
| (21) International Application Number: <b>PCT/AU00/00224</b>  | (81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). |
| (22) International Filing Date: 22 March 2000 (22.03.00)  |  |
| (30) Priority Data:<br>PP 9347 22 March 1999 (22.03.99) AU  |  |
| (71) Applicant (for all designated States except US): RISATEC PTY. LIMITED [AU/AU]; Level 2, 506 Miller Street, Cammeray, NSW 2062 (AU).  |  |
| (72) Inventors; and   |  |
| (75) Inventors/Applicants (for US only): SULLIVAN, Leigh, Albert [AU/AU]; 27 Dalmacia Drive, Wollongbar, NSW 2477 (AU). MCCONCHIE, David, Murray [AU/AU]; 14 Windsor Court, Goonellabah, NSW 2480 (AU). BUSH, Richard [AU/AU]; 20 Fischer Street, Goonellabah, NSW 2480 (AU). | Published<br>With international search report.   |
| (74) Agent: CULLEN & CO.; Level 26, MLC Building, 239 George Street, Brisbane, QLD 4000 (AU).   |  |

(54) Title: APPARATUS FOR ANALYSING REDUCED INORGANIC SULFUR



## (57) Abstract

An apparatus for measuring the reduced inorganic sulfur content of a sample. The apparatus has a reaction chamber (12) and means (14) for introducing a reducing agent that can selectively convert the reduced inorganic sulfur of a sample in the reaction chamber (12) to hydrogen sulfide. The reducing agent can be chromous chloride. The apparatus also includes means for measuring the amount of hydrogen sulfide evolved by reaction of the reducing agent with the sample and a detector for detecting when evolution of the hydrogen sulfide has reduced or ceased. The term "reduced inorganic sulfur" refers to sulfur in a form that can undergo oxidation and includes mineral sulphides and elemental sulfur.

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Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

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| EE | Estonia                  |    |                                       |    |   |    |                          |

## APPARATUS FOR ANALYSING REDUCED INORGANIC SULFUR FIELD OF THE INVENTION

The present invention relates to an apparatus for the quantitative analysis of reduced inorganic sulfur.

5

### BACKGROUND ART

Sulfur is present in the environment in several different forms which may be generally classified as organic and inorganic sulfur. The presence of each form of sulfur has important environmental implications. For example, combustion of both inorganic and organic sulfur produces sulfur dioxide, a greenhouse gas and source of acid rain. Another significant environmental problem is the acid generating potential of a class of inorganic sulfur materials known as reduced inorganic sulfur. These compounds produce acid when materials containing them are mined, excavated or drained, and exposed to atmospheric oxygen.

15

The term "reduced inorganic sulfur" refers to sulfur in a form that can undergo oxidation and includes mineral disulfides (e.g. pyrite and chalcopyrite), monosulfides (e.g. sphalerite, galena and covellite), polysulphides (e.g. pyrrhotite and bornite), non-stoichiometric metal sulfides (e.g. greigite), other sulphides such as chalcocite, sulfites (salts of sulfurous acids) and elemental sulfur. In the present specification and claims the term "reduced inorganic sulfur" will be understood to include any inorganic sulfur compound that can be oxidised.

20

Further types of naturally occurring inorganic sulfur compounds are the sulfate minerals, such as gypsum, which include sulfur in the oxidized sulfate form. These materials are generally not a source of acid in the environment.

30

When sulfide bearing material is mined or excavated, oxidation of the reduced inorganic sulfur may occur. The result is acid sulfate soil and acid mine drainage. Acid mine drainage refers to acid water produced by the oxidation of minerals such as pyrite in the presence of water and is one of the major environmental problems facing the mining industry. The oxidation of reduced inorganic sulfur in acid sulfate soils is a global environmental problem affecting more than 12 million hectares of agricultural land worldwide,

degrading aquatic habitats and corroding concrete and steel infrastructure. It is therefore important for environmental management to be able to measure the amount of reduced inorganic sulfur in a wide range of materials including sediments, soils, mine spoil, sludge, petroleum, mineral ores, fossil fuels and water.

There are several known methods for measuring the sulfur content of a material. Combustion followed by measurement of evolved sulfur oxides is used to measure the total sulfur content (i.e. the combined inorganic and organic sulfur). Such methods are typically used to measure the sulfur content of coal. Combustion of coal is a major source of sulfur dioxide pollution. However, the combustion method does not distinguish between organic sulfur, reduced inorganic sulfur or mineral sulfates and accordingly cannot be used to accurately quantify the reduced inorganic sulfur in a sample.

The most widely used method for assaying reduced inorganic sulfur is by peroxide oxidation in which the sulfur is oxidised to sulfate. The amount of sulfate liberated by peroxide oxidation is then analysed by conventional wet chemical quantitative analysis. Although this method is the accepted procedure, the present inventors have surprisingly and unexpectedly observed that the method is subject to serious interferences from organic sulfur and sulfate minerals such as gypsum. This interference is particularly important when sediments having low reduced inorganic sulfur are measured. An erroneous estimate of the reduced inorganic sulfur content may lead to the recommendation of costly and/or inappropriate and environmentally damaging management practices.

Other methods for analysing reduced inorganic sulfur, but which are considered to be less accurate than the peroxide oxidation method, include:

(a) measuring the total sulfur and soluble sulfur content and estimating the reduced inorganic sulfur content from the difference between the two values. A disadvantage of such differential measurement is that the errors are cumulative.

- (b) microscopic examination of a sample, and
- (c) indirect measurement by estimating the amount of pyritic iron ( $\text{FeS}_2$ ) in a sample. However non-pyritic forms of reduced inorganic sulfur are not measured.

5 It is therefore an object of the present invention to provide a method and apparatus for measuring the reduced inorganic sulfur content of a sample selectively and accurately.

#### DISCLOSURE OF THE INVENTION

According to a first broad form of the invention there is provided  
10 an apparatus for measuring the reduced inorganic sulfur content of a sample, the apparatus having a reaction chamber, means for introducing a reducing agent that can selectively convert the reduced inorganic sulfur of a sample into the reaction chamber to hydrogen sulfide, means for measuring the amount of hydrogen sulfide evolved by reaction of the reducing agent with the  
15 sample and a detector for detecting when evolution of the hydrogen sulfide has reduced or ceased.

The apparatus of the present invention has a reaction chamber for allowing a sample to be tested to be digested by a reducing agent that selectively converts the reduced inorganic sulfur component of a sample to  
20  $\text{H}_2\text{S}$ . The reducing agent should not react with organic sulfur or sulfate materials to produce  $\text{H}_2\text{S}$ . Preferred reducing agents include chromous salts, stannous salts and mercurous salts.

An especially preferred reducing agent is acidified chromous chloride. Acidified chromous chloride solutions are typically prepared by  
25 passing acidified chromic chloride through a column containing zinc, pre-amalgamated in mercuric nitrate. This process is difficult, slow and requires specialised equipment to minimise atmospheric oxidation of the acidified  $\text{CrCl}_2$ . Also, acidified  $\text{CrCl}_2$  is unstable and can only be stored for a few days. Thus, it is preferred that chromous chloride is generated in situ in the reaction  
30 chamber. Typically, chromium, concentrated HCl, ethanol and distilled water are introduced into the reaction vessel. The chromium is typically in the form of a powder, but may also be added as a pellet or slurry.

The reduction reaction is typically carried out in an inert atmosphere such as nitrogen or argon, but can for short periods of time be conducted in air, such as up to about 20 minutes. Generally, the reaction is carried out at elevated temperatures with or without agitation under reflux conditions. The condenser used in the reflux process may be cooled by any of the known methods including a continuous flow of water or a refrigeration unit. In a particularly preferred embodiment of the invention, the apparatus includes a condenser that is cooled by means of water that is recirculated through a refrigeration unit. This arrangement allows for the apparatus to be in the form of a portable unit that is suitable for use in the field.

10 The apparatus of the invention is typically automated and controlled by a central processor which can control some, or essentially all, of the functions of the apparatus. This allows the apparatus to be operated by non-skilled personnel.

15 Typically, the amounts of reagents added to the reaction chamber are automatically supplied to the reaction chamber in pre-determined quantities in a pre-determined order. Generally, the liquid ingredients are added using a peristaltic pump.

20 In a further broad form of the present invention there is provided an automated apparatus for measuring the reduced inorganic sulfur content of a sample, the apparatus having a reaction chamber, means for heating the chamber, a condenser, means for introducing a reducing agent into the reaction chamber which converts reduced inorganic sulfur to hydrogen sulfide and measuring means for measuring the amount of hydrogen sulfide evolved.

25 Typically, the apparatus includes a refrigeration unit for cooling water for the condenser.

The reduced inorganic sulfur composition of the sample may be calculated from the amount of H<sub>2</sub>S evolved by reaction with the reductant. The H<sub>2</sub>S evolution may be measured by any of the known methods of 30 measuring H<sub>2</sub>S. Such methods include colourimetric, turbidimetric and gravimetric methods. Particularly preferred methods include electrochemical, spectroscopic or chromatographic techniques such as mass spectroscopy,

gas chromatography, UV or IR spectroscopy. A particularly preferred measurement means is an electrochemical gas analyser. Generally, the gas which provides the atmosphere in the reaction chamber also serves as a carrier gas to carry the evolved H<sub>2</sub>S to the measurement means.

5 The amount of H<sub>2</sub>S evolved may also be measured indirectly. For example, H<sub>2</sub>S may be oxidised to sulfate or sulfur dioxide. These oxidation products may then be measured by suitable methods including turbidimetric or gravimetric, chromatographic or spectroscopic methods.

10 The apparatus of the present invention typically includes a means for detecting when the evolution of H<sub>2</sub>S has decreased to a pre-determined rate. Typically, this is when H<sub>2</sub>S evolution has substantially ceased. Cessation of H<sub>2</sub>S evolution indicates that the reduction reaction has been completed. When completed, a fresh sample may be analysed. With conventional wet chemical procedures, a sample is allowed to react for a pre-determined maximum length of time. The present inventors have observed 15 that the reduction reaction can often take much less time than has traditionally been allowed. Thus, by being able to monitor when the reaction has ceased, sample throughput may be optimised. The apparatus may include an alarm or other signalling device to alert an operator that the reaction has finished.

20 Alternatively and/or in addition to, the apparatus may have means for automatically disengaging any heating of the reaction chamber and deactivate the condenser on completion of the reduction reaction.

25 The means for detecting when evolution of H<sub>2</sub>S has ceased may be in addition to, or part of, the H<sub>2</sub>S measuring means. For example a gas sensor or other detection means may be associated with the reaction chamber to detect the H<sub>2</sub>S therein. Gas sensors for detecting the presence of H<sub>2</sub>S are known.

30 In the preferred embodiment where the H<sub>2</sub>S measurement means is an electrochemical gas analyser or spectrophotometric analyser, the analyser may be programmed to detect when the rate of H<sub>2</sub>S evolution has decreased.

Preferably the electrochemical gas analyser can measure the

H<sub>2</sub>S concentration on a real time basis to allow the rate of H<sub>2</sub>S evolution to be constantly monitored. Typically, the H<sub>2</sub>S evolution data may be represented as a function of cumulative H<sub>2</sub>S concentration v time or absolute H<sub>2</sub>S concentration v. time.

5        Different forms of reduced inorganic sulfur react at different rates. Thus, by being able to monitor the rate of H<sub>2</sub>S evolution, information can be obtained as to the relative amounts of different forms of reduced sulfur materials present in the sample.

10      According to a further broad form of the invention there is provided an apparatus for measuring the amount of reduced inorganic sulfur in a sample, the apparatus having a reaction chamber, a means of introducing a reducing agent that can selectively convert the inorganic reduced sulfur of the sample in the reaction chamber to hydrogen sulfide and means for continually monitoring the amount of hydrogen sulfide evolved.

15      According to still a further broad form of the invention there is provided a method of measuring the amount of reduced inorganic sulfur in a sample, the method including reacting a sample with a reducing agent that selectively converts the reduced inorganic sulfur to hydrogen sulfide and measuring hydrogen sulfide evolved as a function of time.

20      The ability to determine the relative amounts of different types of reduced inorganic sulfur is important for environmental management. This enables predictions to be made as to the potential rate of acid generation as opposed to simply calculating the total acid generating potential of a soil material.

25      A knowledge of a form of sulfur generally referred to as acid volatile inorganic sulfur is of particular importance. Acid volatile sulfur includes monosulfides and non-stoichiometric sulphides such as greigite and mackinawite. In the preferred apparatus in which acidic chromous chloride is generated *in situ*, the sample can be treated with the concentrated HCl and 30 ethanol only. Neither chromium nor water are added.

Only the acid volatile sulfur fraction will react under these conditions and can thus be selectively analysed. If the total reduced inorganic

sulfur is required, the same sample can then be treated with the chromous chloride reductant by introducing chromium powder and water into the reaction chamber as described above.

#### BRIEF DESCRIPTION OF THE DRAWINGS

5       Figure 1 schematically illustrates a preferred apparatus of the present invention, and

Figure 2 illustrates a further preferred apparatus of the present invention.

#### BEST MODE

10       The apparatus of both Figures 1 and 2 are designed to be fully automated and to be portable to allow onsite use in the field.

15       The apparatus 11 illustrated in Figure 1 has a removable reaction vessel 12. An operator can place a known volume or mass of a sample to be tested into the reaction vessel. Alternatively, the apparatus can include an in-built balance to measure the mass of material in the reaction chamber. The reaction vessel 12 is placed in a heating mantle 13 which is equipped with a magnetic stirrer. In use, the reaction vessel is connected, with an air-tight seal, to inlets 14, 15 and outlet 16. The sealed connection may be provided by any suitable means such as ground glass joints or O ring seals.

20       The inlet 14 is connected to a chromium powder dispenser 17. The inlet 15 is connected, with an air-tight seal, to a nitrogen gas source 18 and to acid and water and ethanol reservoirs 19, 20. The reservoirs 19, 20, 21 each have a peristaltic pump 22, 23, 24 for delivering pre-determined amounts of liquids via three way valves to inlet 15. The outlet 16 is connected to an insulated condenser 26 which typically has copper pipes surrounding a glass core. Refrigerant is supplied to the condenser 26 from pump 27. Typically, the apparatus includes a heat exchange apparatus by which heat extracted from the condenser can be used to heat the mantle 13. The upper 25 end of the condenser 26 is connected, via an air-tight seal, to an IR gas analyser 28. A moisture control unit 29 is disposed between condenser and analyser 28.

The apparatus is operated by a central control computer 30. The power source 31 is typically a 12V power supply. However, mains supply of any voltage (e.g. 110V or 240V), AC or DC, may be used by the incorporation of a suitable adaptor.

5 To operate the apparatus, an operator places an amount of a sample to be tested in the reaction chamber and places the chamber in the mantle. Prior to analysis, the reservoirs of the chamber are charged with chromium powder, ethanol, water and concentrated HCl respectively. The sample to be tested may be any material containing reduced inorganic sulfur  
10 and includes soil, mine spoil, fossil fuels such as coal and oil, sediments, plants and animal materials, water (both naturally occurring and waste), chemical waste and minerals. The samples may be pretreated depending on the nature of the sample. For example the mineral samples may be fine ground prior to analysis.

15 The apparatus is operated by the computer 30 which can be programmed to fully automate the analysis. If desired manual override capabilities may be included. Under normal operational conditions, all that is required of the operator after placement of the sample in the reaction chamber is to press an "on" switch. This will initiate purging of the system  
20 with nitrogen for a pre-determined and monitored flow rate. After a fixed time, pre-determined amounts of chromium powder, water, ethanol and 12N HCl are added to the reaction chamber in turn. The water also serves to flush the HCl from the lines.

25 The amounts of reagent added will depend on the weight of the sample. For a 1g sample, typically about 2.059g chromium powder, 10mL ethanol, 28.25mL of 12N HCl and 31.75mL of water are added.

After addition of the reagents, the reaction chamber is heated to boiling with stirring. As H<sub>2</sub>S is evolved it is carried by the nitrogen through the dessicant in the moisture trap 29 to the IR gas analyser 28. The cumulative  
30 concentration of the H<sub>2</sub>S gas is calculated by the computer 30 using an algorithm relating H<sub>2</sub>S concentration and gas flow rate. When H<sub>2</sub>S evolution has ceased or fallen below a pre-determined level the computer will terminate

the analysis by sequentially disengaging the electrochemical gas analyser, and turning off the heating mantle 13, gas flow and condenser 26. The reaction vessel 12 can then be removed by the operator and cleaned. The apparatus is ready for the next analysis.

5 The total amount of reduced inorganic sulfur can be read directly from a digital panel or stored digitally. The results may also be presented graphically as either cumulative H<sub>2</sub>S production or real time H<sub>2</sub>S production rates.

10 The apparatus of Figure 2 is similar to that illustrated in Figure 1 and the same reference numerals refer to the same features.

The apparatus does not include an ethanol reservoir. Ethanol is instead added to reaction vessel 12 together with a sample for analysis. The nitrogen inlet of Figure 1 has been replaced by a pump 35 to introduce air as the carrier gas. The condensor 26 is cooled by water pumped from 15 refrigeration unit 36 via pump 27. The IR analyser has been replaced by an electrochemical gas analyser 37. A H<sub>2</sub>S trap 38 is located between the analyser and vent 39.

20 The above procedures may be modified to separately analyse the acid volatile sulfur fraction. In this case, the sample and ethanol are placed in the reaction chamber as before, but only HCl (20mL) is added. The heating mantle is not required and remains turned off. If both the acid volatile and total reduced sulfur are required, the first procedure may then be performed on the sample remaining in the reaction chamber. However, it will 25 only be necessary to add 8.25mL of HCl (because 20mL have already been added) plus the chromium powder and water.

It can be seen that the apparatus of the present invention can 30 provide a self contained, portable and automated analyser for reduced inorganic sulfur. At present there is no automated system for quantifying reduced inorganic sulfur. All existing techniques used by industry must be performed by skilled personnel in a well equipped laboratory. Thus, it has hitherto not been possible to analyse reduced inorganic sulfur on site. Automation of the present apparatus allows onsite analysis. Further, skilled

laboratory personnel are not required to conduct the analysis.

The present apparatus can be in the form of a completely portable unit which may be operated from a 12V power supply. The present apparatus can also be operated using a mains power supply in the laboratory.

- 5 The use of recirculated chilled water contributes to the ability of the apparatus to be self contained. Such portability and self containment is not practical with conventional wet chemistry techniques.

The ability to constantly monitor H<sub>2</sub>S evolution and to detect when such evolution ceases also offers significant advantages over wet 10 chemical analytical techniques in which a sample is digested for a set period of time. The present inventors have observed that for some samples, digestion can be completed in about 10 minutes as compared to the standard time of one hour allowed for reaction. Thus by monitoring completion of the reaction, the speed of analysis can be considerably increased.

- 15 The present invention also provides a method and apparatus for selectively measuring the reduced inorganic sulfur without interference from organic sulfur and sulfate materials. Still further, the acid volatile sulfur fraction can be selectively measured. Also, by monitoring the rate of hydrogen sulfide evolution, important information can be obtained as to the relative 20 amounts of different types of reduced inorganic sulfur in the sample.

It will be appreciated that various changes and modifications may be made to the embodiments as described and claimed herein without departing from the spirit and scope of the invention.

## CLAIMS

1. An apparatus for measuring the reduced inorganic sulfur content of a sample, the apparatus having a reaction chamber, means for introducing a reducing agent that can selectively convert the reduced inorganic sulfur of a sample in the reaction chamber to hydrogen sulfide, means for measuring the amount of hydrogen sulfide evolved by reaction of the reducing agent with the sample and a detector for detecting when evolution of the hydrogen sulfide has reduced or ceased.  
5
2. The apparatus of claim 1, which includes a reservoir for storing a reducing agent or a precursor thereof and the reducing agent is selected from the group consisting of Cr(II), Sn(II) and Hg(II)  
10
3. The apparatus of claim 2, wherein the reducing agent is chromous chloride.  
15
4. The apparatus of claim 3, which includes means for introducing predetermined amounts of chromium powder and hydrochloric acid into the reaction chamber such that chromous chloride can be generated in the reaction chamber.  
20
5. The apparatus of claim 1, which further includes a source of hydrochloric acid and means for introducing the acid into the reaction chamber prior to introduction of the reducing agent such that the amount of any acid volatile sulfur in the sample can also be measured.  
25
6. The apparatus of claim 1 which includes a source of a carrier gas for introduction into the reaction chamber and the carrier gas can carry any evolved hydrogen sulfide to the measurement means.  
30
7. The apparatus of claim 6, wherein the carrier gas is air and the apparatus includes a pump for pumping air into the reaction chamber.
8. The apparatus of claim 6, wherein the carrier gas is an inert gas and the apparatus includes a supply of the inert gas.
9. The apparatus of claim 1, which includes means for heating the reaction chamber.  
35
10. The apparatus of claim 9, which includes a condenser fluidly connected to the reaction chamber and a source of refrigerated fluid for  
40

cooling the condenser.

11. The apparatus of claim 10, which includes means for deactivating the heating means and source of refrigerated fluid when evolution of hydrogen sulfide has ceased.
- 5 12. The apparatus of claim 1 which includes a central control unit for controlling the introduction of the reducing agent and any other reagents to the reaction chamber.
13. The apparatus of claim 10, wherein the control unit includes means for calculating the amount of reduced inorganic sulfur in the sample
- 10 from the measured sulfur hydroxide.
14. The apparatus of claim 1, which includes a means for signalling when evolution of hydrogen sulfide has ceased.
15. The apparatus of claim 1 wherein the measuring means detects when hydrogen sulfide evolution has ceased.
16. The apparatus of claim 14 wherein the means for measuring evolved hydrogen sulfide is selected from the group consisting of an IR spectrometer, a UV spectrometer, a gas chromatograph, and an electrochemical gas analyzer.
17. The apparatus of claim 16, wherein the measurement means
- 20 continuously measures the hydrogen sulfide evolved.
18. The apparatus of claim 1 which further includes means for oxidising the hydrogen sulfide evolved and measuring the amount of oxidised hydrogen sulfide.
19. The apparatus of claim 1, wherein the sample is selected from
- 25 the group consisting of sediment, soil, sludge, petroleum, mine spoil, coal, oil, water, plant, animal and mineral material.
20. The apparatus of claim 19, wherein the sample includes organic sulfur and/or a mineral sulfate.
21. The apparatus of claim 19, which is in the form of a portable unit.
- 30 22. A method of measuring the amount of reduced inorganic sulfur in a sample, the method including reacting a sample with a reducing agent that selectively converts the reduced inorganic sulfur to hydrogen sulfide and

measuring the hydrogen sulfide evolved as a function of time.

23. The method of claim 22, wherein the reducing agent is selected from the group consisting of Cr(II), Sn(II) and Hg(II).

24. The method of claim 23, wherein the reducing agent is  
5 chromous chloride.

25. The method of claim 22, wherein means for securing the hydrogen sulfide evolved is selected from an IR spectrometer, a UV spectrometer, a gas chromatograph, and an electrochemical gas analyzer.

26. The method of claim 22, wherein the sample is selected from the  
10 group consisting of sediment, soil, sludge, petroleum, mine spoil, coal, oil, water, plant, animal or mineral material.

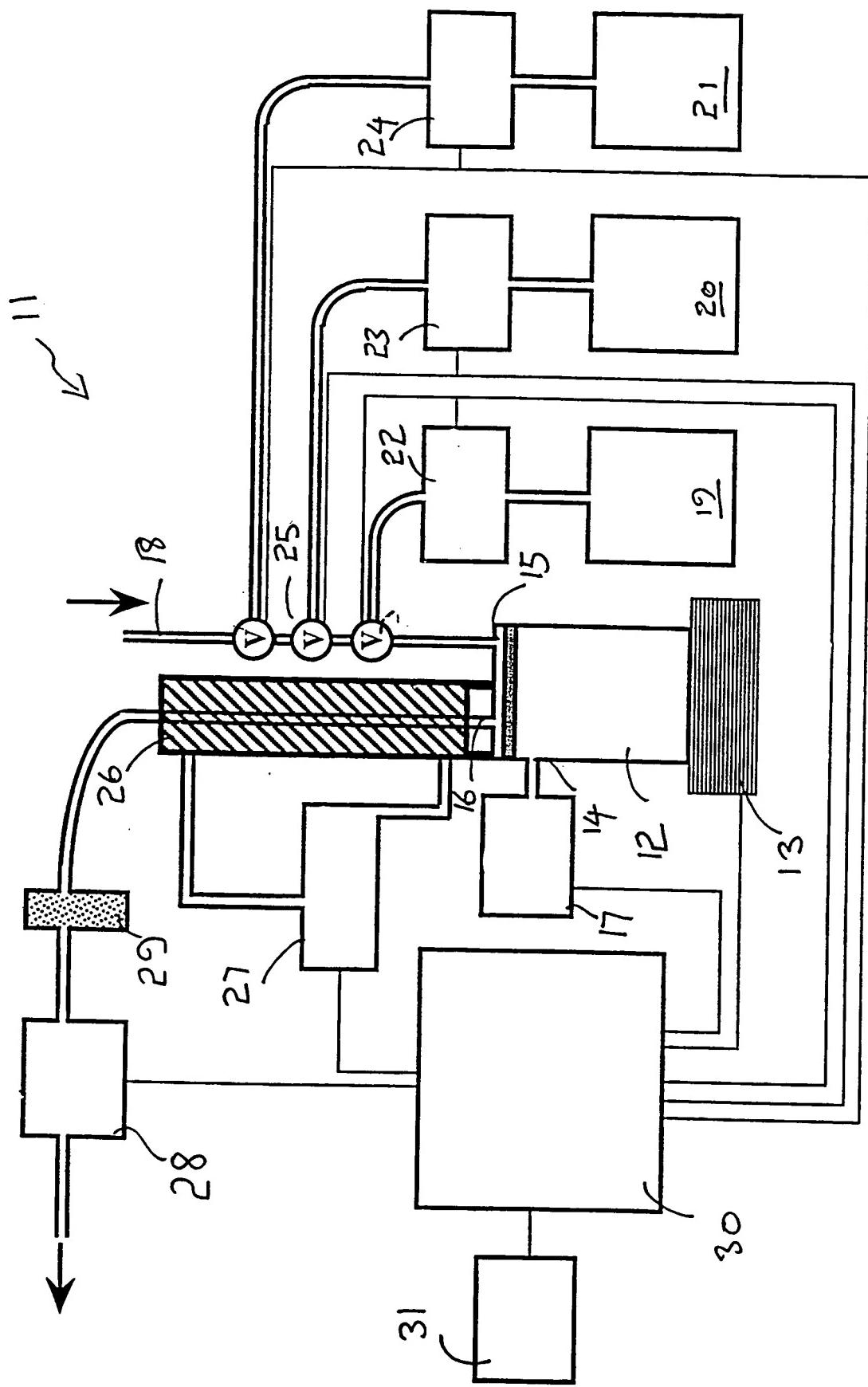


Fig. 1

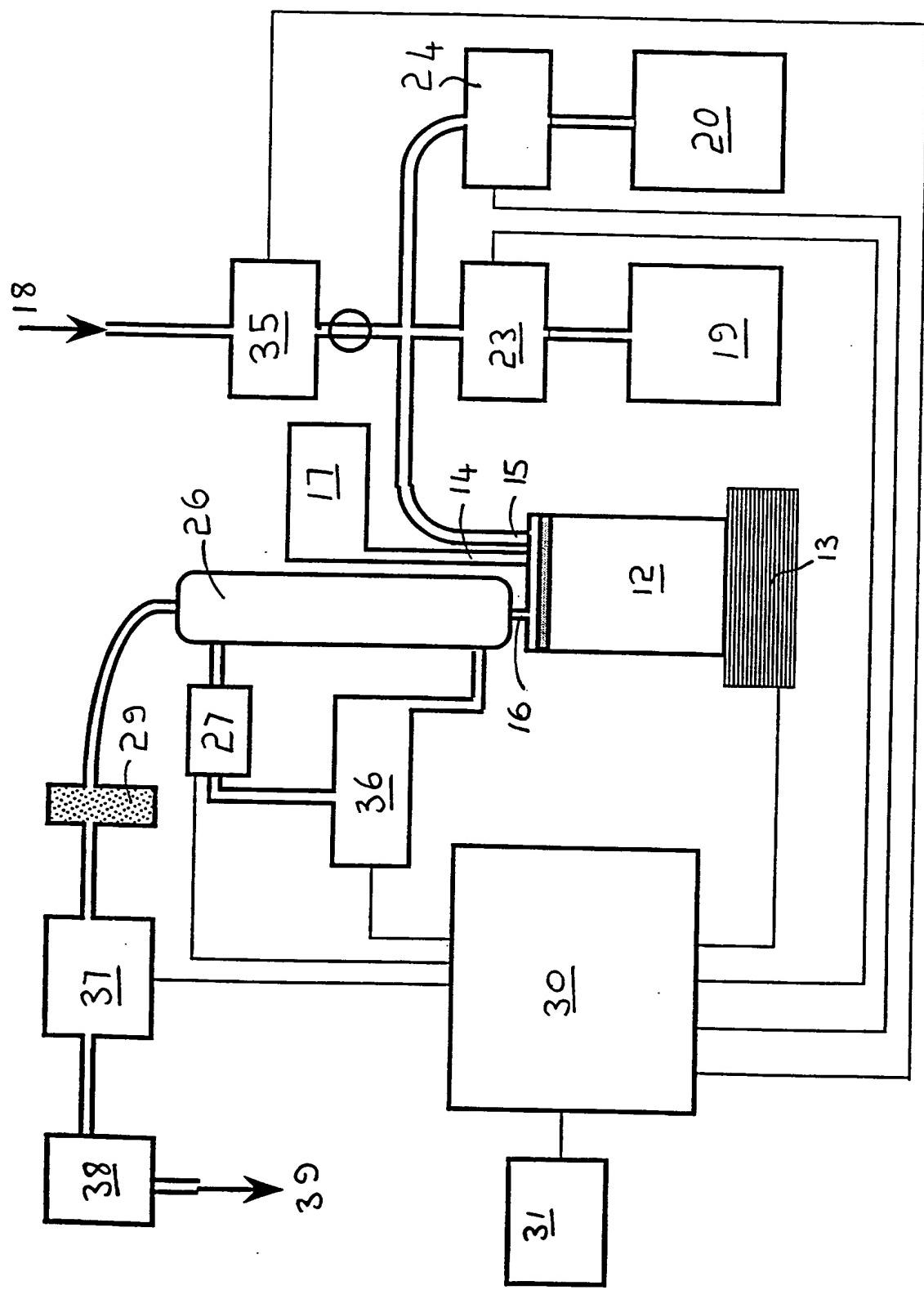


Fig. 2

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/AU00/00224

| <b>A. CLASSIFICATION OF SUBJECT MATTER</b>   |  |   |
|--|--|---|
| Int. Cl.?: G01N 31/00  |  |   |
| According to International Patent Classification (IPC) or to both national classification and IPC  |  |   |
| <b>B. FIELDS SEARCHED</b>  |  |   |
| Minimum documentation searched (classification system followed by classification symbols)<br>G01N  |  |   |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  |  |   |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)<br>DWPI and JAPIO with keywords: sulf(ph)ur, 'hydrogen sulf(ph)ide', H <sub>2</sub> S, mineral, meas+, assay, analy+  |  |   |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>  |  |   |
| Category*  | Citation of document, with indication, where appropriate, of the relevant passages                                 | Relevant to claim No.   |
| A  | Derwent Abstracts Accession No. 91-162504/22, Class S03,<br>SU 1578-672 A (GEOCHEM MIN) 15 July 1990               |   |
| A  | Derwent Abstracts Accession No. 97-090521/09, Class J04 M24,<br>JP 08327625 A (NIPPON STEEL CORP) 13 December 1996 |   |
| <input type="checkbox"/> Further documents are listed in the continuation of Box C <input type="checkbox"/> See patent family annex  |  |   |
| * Special categories of cited documents:<br>"A" document defining the general state of the art which is not considered to be of particular relevance<br>"E" earlier application or patent but published on or after the international filing date<br>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br>"O" document referring to an oral disclosure, use, exhibition or other means<br>"P" document published prior to the international filing date but later than the priority date claimed |  |   |
| Date of the actual completion of the international search<br>17 May 2000   |  | Date of mailing of the international search report<br>29 MAY 2000             |
| Name and mailing address of the ISA/AU<br>AUSTRALIAN PATENT OFFICE<br>PO BOX 200, WODEN ACT 2606, AUSTRALIA<br>E-mail address: pct@ipaaustralia.gov.au<br>Facsimile No. (02) 6285 3929   |  | Authorised officer<br><br><b>ROSS BURDON</b><br>Telephone No : (02) 6283 2605 |